

R70-71<sup>2</sup>  
TECHNICAL LIBRARY  
U. S. ARMY  
NATICK LABORATORIES  
NATICK, MASS. 01760

## **The X-Ray Crystallographic Determination of the Structure of Gynocardin**

By H. S. KIM, G. A. JEFFREY,\* and D. PANKE

*(The Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15213 and the Biocrystallography Laboratory of the Veterans Administration Hospital, Pittsburgh, Pennsylvania 15240)*

Reprinted from

# **Chemical Communications 1970**

The Chemical Society, Burlington House, London W1V 0BN

## The X-Ray Crystallographic Determination of the Structure of Gynocardin

By H. S. KIM, G. A. JEFFREY,\* and D. PANKE

(The Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15213 and the Biocrystallography Laboratory of the Veterans Administration Hospital, Pittsburgh, Pennsylvania 15240)

and R. C. CLAPP, R. A. COBURN, and L. LONG, JUN.

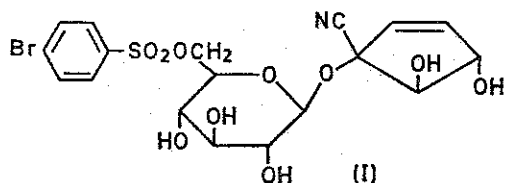
(Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760)

**Summary** The X-ray structure determination of 6-O-brosylgynocardin is reported.

A STRUCTURE containing a cyclopentenoid nucleus has been suggested<sup>1</sup> for gynocardin, a cyanogenetic glucoside first

isolated from seeds of *Gynocardia odorata* R.Br.<sup>2</sup> Recent studies<sup>3</sup> have implicated amino-acids as biogenetic precursors of the cyanogenetic glucosides, and the unusual structure suggested for gynocardin has therefore aroused interest in the nature of a possible amino-acid precursor.<sup>4,5</sup>

We now report proof of the suggested structure by an X-ray crystallographic structure determination of the 6-O-brosyl (*p*-bromobenzenesulphonyl) derivative of the glucoside, (I). The configurations at C(1) and C(3) of the cyclopentene ring, which were not previously determined, have been established.



Because of difficulties in acquiring additional *Gynocardia odorata* seeds, seeds of *Pangium edule* Reinw., collected in Laguna, Republic of the Philippines, were used as a source of gynocardin for this work. Gynocardin has been reported to occur in *Pangium edule* by De Jong<sup>6</sup> and Brill.<sup>7</sup> Chemical and spectral data obtained in the present study verify the identity of the cyanogenetic glucoside from this source with that isolated from *Gynocardia odorata*. The brosyl derivative,  $C_{18}H_{26}BrNO_{10}S$ , was prepared by treatment of gynocardin with *p*-bromobenzenesulphonyl chloride in pyridine. Elemental analysis and spectral data (i.r. and n.m.r.) of crystals obtained from acetone showed that a molecule of acetone was present as solvent of crystallization.

The X-ray diffraction data were obtained on a Picker diffractometer using Cu- $K_{\alpha}$  radiation from needles elongated

about the *b* axis. Crystal data:  $a = 18.472$ ,  $b = 6.329$ ,  $c = 11.278$  Å,  $\beta = 106.25^{\circ}$ ,  $U = 1265.83$  Å<sup>3</sup>,  $M = 580.42$ ,  $D_c = 1.523$ ,  $D_m = 1.528$  g cm<sup>-3</sup>, at 19°,  $Z = 2$ , space group  $P2_1$  from systematic extinctions  $0k0$  absent for  $k$  odd. Of 1094 intensities measured, 367 were not significantly greater than background.

The atomic co-ordinates of the bromine and sulphur atoms were derived from a sharpened three-dimensional  $F^2$  synthesis. The remainder of the structure was determined, with some difficulty, by successive Fourier synthesis and least-squares refinement. The rapid fall-off of intensities with  $\sin \theta$  reduced the effectiveness of the sulphur scattering for distinguishing between the mirror images of the structure phased on the bromine atoms. The final agreement index was 0.10 with anisotropic temperature factors. The cyclopentene ring is attached to the O(1) of  $\beta$ -glucose. The absolute configuration was not determined since it has been proved that the  $\beta$ -glucose has the D, C1 conformation.<sup>1,8</sup> The cyano-group at C(1) is *cis* to the hydroxyl at C(2) and *trans* to that at C(3). In its relationship to chaulmoogric acid,<sup>9</sup> the cyano and glucose units replace the tridecanoic acid and hydrogen respectively.†

The electron density distribution of the acetone of crystallization was poorly resolved and the atomic positions were ill-defined. It would appear that the solvent molecules in the crystal are disordered and possibly non-stoichiometric. The molecules are associated by intermolecular hydrogen-bonding between the hydroxy-groups.

(Received, January 8th, 1970; Com. 032.)

† A table of atomic positional co-ordinates and a diagram of the molecular conformation are available on request.

<sup>1</sup> R. A. Coburn and L. Long, jun., *J. Org. Chem.*, 1966, **31**, 4312.

<sup>2</sup> F. B. Power and F. H. Gornall, *Proc. Chem. Soc.*, 1904, **20**, 137.

<sup>3</sup> For a review, see E. E. Conn and G. W. Butler in "Perspectives in Phytochemistry," eds. J. B. Harborne and T. Swain, Academic Press, London, 1969, ch. 2.

<sup>4</sup> E. E. Conn, *J. Agric. Food Chem.*, 1969, **17**, 519.

<sup>5</sup> M. G. Ettlinger and A. Kjaer in "Recent Advances in Phytochemistry," eds. T. J. Mabry, R. E. Alston, and V. C. Runeckles, Appleton-Century-Crofts, New York, 1968, vol. 1, p. 127.

<sup>6</sup> A. W. K. De Jong, *Rec. Trav. chim.*, 1909, **28**, 24; 1911, **30**, 220.

<sup>7</sup> H. C. Brill, *Philippine J. Sci.*, 1917, **12**, 37.

<sup>8</sup> F. B. Power and F. H. Lees, *J. Chem. Soc.*, 1905, **87**, 349.

<sup>9</sup> K. Mislow and I. V. Steinberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3807.